Premelting of Long *n*-Paraffins in Chain-Extended Lamellae. An Electron Diffraction Study

Douglas L. Dorset*

Electron Diffraction Department, Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, New York 14203

Rufina G. Alamo and Leo Mandelkern

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306

Received May 7, 1992; Revised Manuscript Received August 3, 1992

ABSTRACT: Electron diffraction is used to study the thermally-induced structural changes in *n*-paraffins for which chains are too long to permit transition to a hexagonal layer packing. Monolamellar crystals of n-$C_{50}H_{102}$, n-$C_{60}H_{122}$, n-$C_{82}H_{166}$, and n-$C_{94}H_{190}$ obtained from dilute solution undergo a lattice expansion upon heating so that the lateral orthorhombic unit cell axial ratio approaches a limiting value $a/b \simeq 1.55$. Near the melting point, a structure with an oblique chain packing begins to form irreversibly. Crystallization from the melt forms the monoclinic structure described earlier by Khoury. Diffraction patterns from heated epitaxially-crystallized samples demonstrate that the longitudinal chain motions responsible for this transition occur well below the melting point, producing a slightly thickened lamellar structure which, on average, resembles a pure paraffin with one more chain methylene unit. This structure incorporates the expected interfacial disorder due to conformational defects.

Introduction

Because of the several applicable entropic contributions to melting,[1] *n*-paraffins are well-known examples of molecular compounds which exhibit premelting behavior. In addition to the crystal–crystal transition to the hexagonal chain packing in individual lamellae, which occurs for odd and even paraffins within certain length limitations,[2] other phenomena have been observed which seem to have no dimensional restrictions and therefore may be more important for understanding the melting behavior of the infinite-chain polymer.

Starting with the early work of Müller,[3] it is clear that lateral expansion of the crystalline lattice occurs for all heated paraffins, whether or not the hexagonal layer packing results. For all even paraffins we have found that this gradual expansion seems to reach a limiting value before the abrupt crystal–crystal transition takes place.[4]

As indicated by early measurements of chain torsional freedom,[5] chain twists in the form of conformational defects are also important, leading often to a sequence of microstates with increasing temperature. Vibrational spectroscopic measurements demonstrate[6] that the largest number of such defects is found near the chain ends and that the form of the disorders is the same whether or not the chain length will allow the hexagonal layer packing to be formed at higher temperature.[7] This has been independently demonstrated by solid-state carbon-13 NMR measurements.[8,9] This accumulation of defects at lamellar interfaces is manifested in diffraction experiments by changes in resolution and intensity of the low-angle reflections. For example, electron density models have been proposed for the lower alkanes,[10] such as n-$C_{21}H_{44}$, as well as the higher ones,[11,12] e.g., n-$C_{94}H_{190}$, to explain the same phenomenon. Similarly, electron diffraction measurements have made it possible to visualize this lamellar disordering in single crystals of n-$C_{36}H_{74}$.[13]

The third expression of thermally-induced chain-end disorder has been the presence of longitudinal motions along the major chain axes. By microscopy, it is observed to occur for the shorter odd- and even-chain alkanes, as well as the longer ones, since ridged corrugations are found in the heated crystalline lozenges.[14-16] For longer chains which do not transform to the hexagonal phase, this longitudinal movement seems to be the major consequence of the gradual accommodation of chain-end conformational disorder when the crystals are heated toward the melting point.[12] One also notes a change in lamellar spacing with increasing temperature.[16] In addition, the presence of longitudinal chain disorder seems to be the best way to account for continuous diffuse scattering intensity in electron diffraction patterns taken from *n*-alkanes or polyethylene crystallized by epitaxial orientation of a cooled melt.[7]

While the importance of the chain-end disorder mechanisms becomes clear, some of the experimental observations are somewhat equivocal—because they are either indirect indications or based on measurements of bulk samples where several states can simultaneously coexist. This paper will demonstrate the major forms of extended-chain lamellar packing disorder for the *n*-paraffins ≥ n-$C_{40}H_{82}$ in terms of single-crystal diffraction patterns.

Materials and Methods

***n*-Paraffins.** Samples of n-$C_{50}H_{102}$ and n-$C_{60}H_{122}$, both with an advertised purity of 99% (and demonstrated by sharp melting transitions), were purchased from Fluka AG (Buchs, Switzerland). Thermal data for these paraffins were published earlier.[18] The n-$C_{82}H_{166}$ sample was a gift from Dr. John R. Fryer, University of Glasgow, Glasgow, U.K. The melting point agrees with the value listed by Broadhurst.[19] The longest chain studied, n-$C_{94}H_{190}$, is the same paraffin sample studied by Fischer[12] and others,[20] and its melting temperature has been reported.[19,20]

Crystallization was carried out in two ways. To prepare lozenge-type crystallites, a dilute solution was made in a warm solvent (e.g., light petroleum or toluene) and the (mostly) monolamellar crystals formed as a drop of solution was cooled in a carbon-film-covered electron microscope grid. In the other method, epitaxial crystallization of the shortest paraffin n-$C_{50}H_{102}$ was carried out by Dr. W. P. Zhang using a somewhat complicated procedure.[21] After deposition of the paraffin from the vapor phase onto a freshly-cleaved KCl substrate, it was annealed in the presence of this substrate to produce a stable lamellar structure, as described earlier. Upon coating with a thin carbon film, the epitaxially-oriented samples were freed from the

0024-9297/92/2225-6284$03.00/0

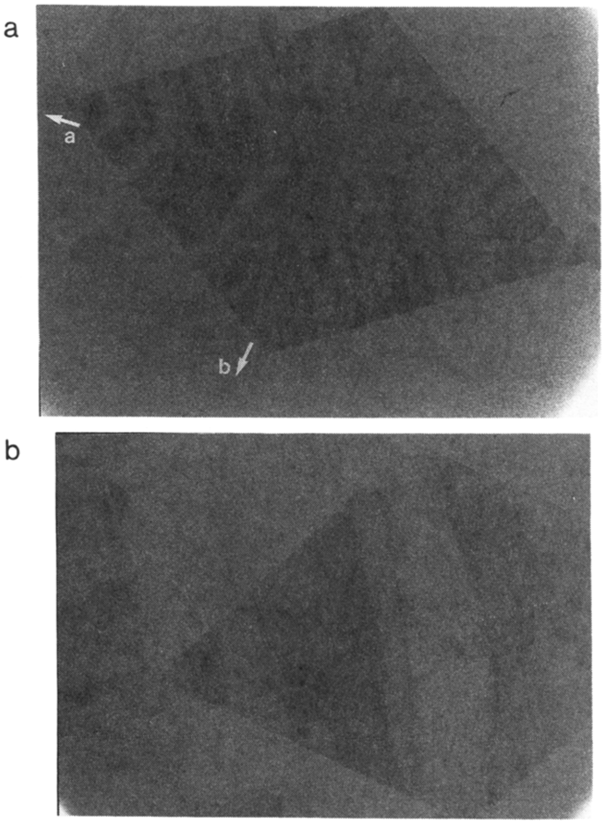

Figure 1. Bright-field electron microscope images of monolamellar $n\text{-}C_{94}H_{190}$ lozenges: (a) solution-crystallized form showing sectorization; (b) heated crystal showing bend contour bands along [010]. The unit cell axial directions for the orthorhombic structure are indicated.

substrate by floating the film onto a water surface and picking these up with bare copper electron microscope grids.

Experiments in the Electron Microscope. The instrument used for this work was a JEOL JEM-100CXII electron microscope operated at 100 kV. Low electron beam doses were used at all times to ensure that the samples would not be damaged by inelastically scattered electrons while the useful elastically scattered information was being recorded. This requires the control of illumination levels with the condenser lens and use of a fast photographic emulsion such as Kodak DEF-5 X-ray film to record the selected area electron diffraction patterns or bright film electron microscope images (at a direct $10^4\times$ magnification). There were no salient perturbations to these data due to beam damage.

Heating experiments in the electron microscope were made possible with a Gatan 626 sample stage which permits maintenance of the paraffin crystals at temperatures up to 150 °C with a stability within 1 °C.

Results

Paraffin Crystals. As described earlier,[22,23] *n*-paraffins with chain lengths longer than 40 carbons, when crystallized according to the recipe given above, form orthorhombic lozenges which exhibit sectorization behavior in bright-field electron micrographs. The upper limit investigated in these studies[23] was $n\text{-}C_{82}H_{166}$. A further example is given for $n\text{-}C_{94}H_{190}$ (Figure 1a). As in polyethylene, the alternate bright and dark bands indicate chain packings which, respectively, are either slightly oblique or untilted orientations of the long axes (e.g., results[23] of high-resolution "lattice images" from $n\text{-}C_{82}H_{166}$). The crystallographic planes are the same as those involved in polyethylene sectorization,[24] but their orientation in each sector is nearly orthogonal to the direction found in the chain-folded polymer crystals. Although an oblique chain packing, related to the $R(\pm1,\pm1)$ layers proposed by Kitaigorodskii[25] for polymethylene chains, must be responsible for the crystal nucleation as a 4-fold twin, the corrugations in Figure 1 are not extreme enough to be detected via surface decoration by a fine metal coating. Hence, the resultant angular misorientation of the chain axes must be less than a couple degrees.

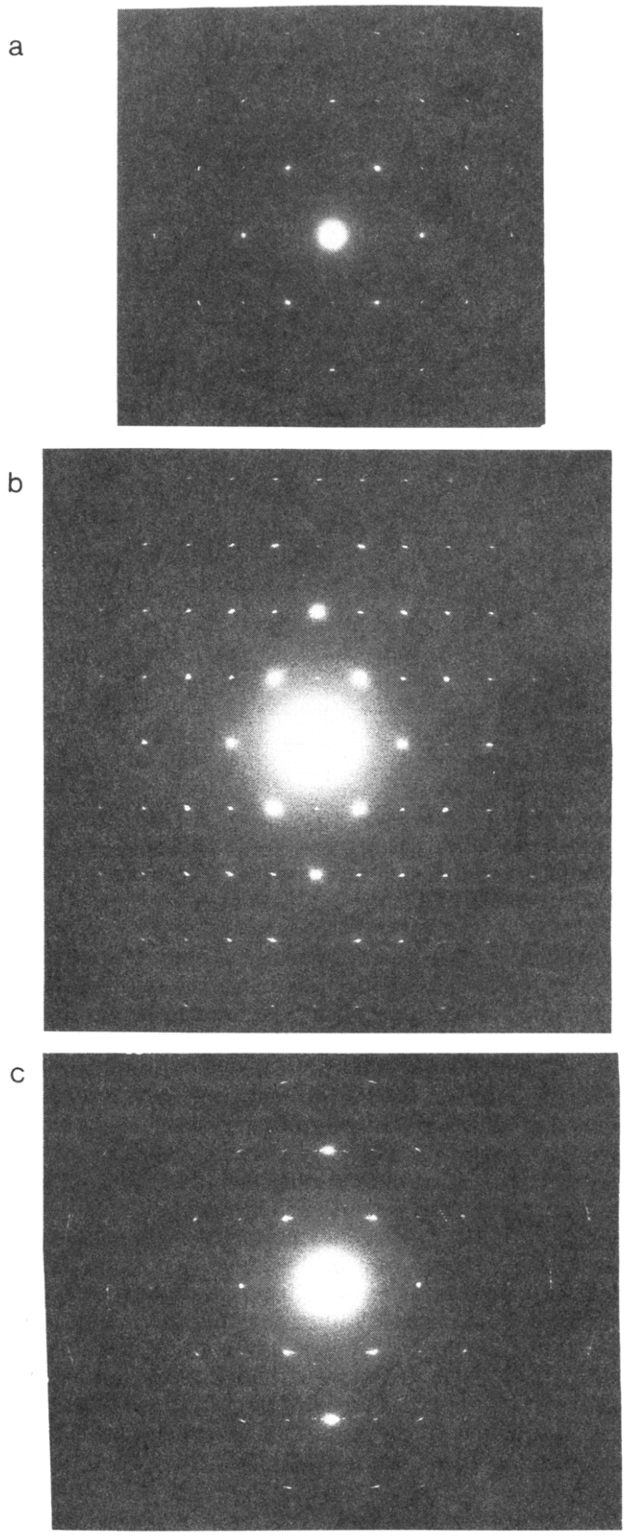

Figure 2. Electron diffraction patterns from $n\text{-}C_{94}H_{190}$: (a) low-temperature form characteristic of the orthorhombic layer (see Teare[35] or Dorset[36] for discussion of the layer symmetry of the orthorhombic structure); (b) higher temperature form obtained 1 °C below the melting point (chain tilt is indicated around the $b = 4.96$ Å axis; (c) sample crystallized from the melt.

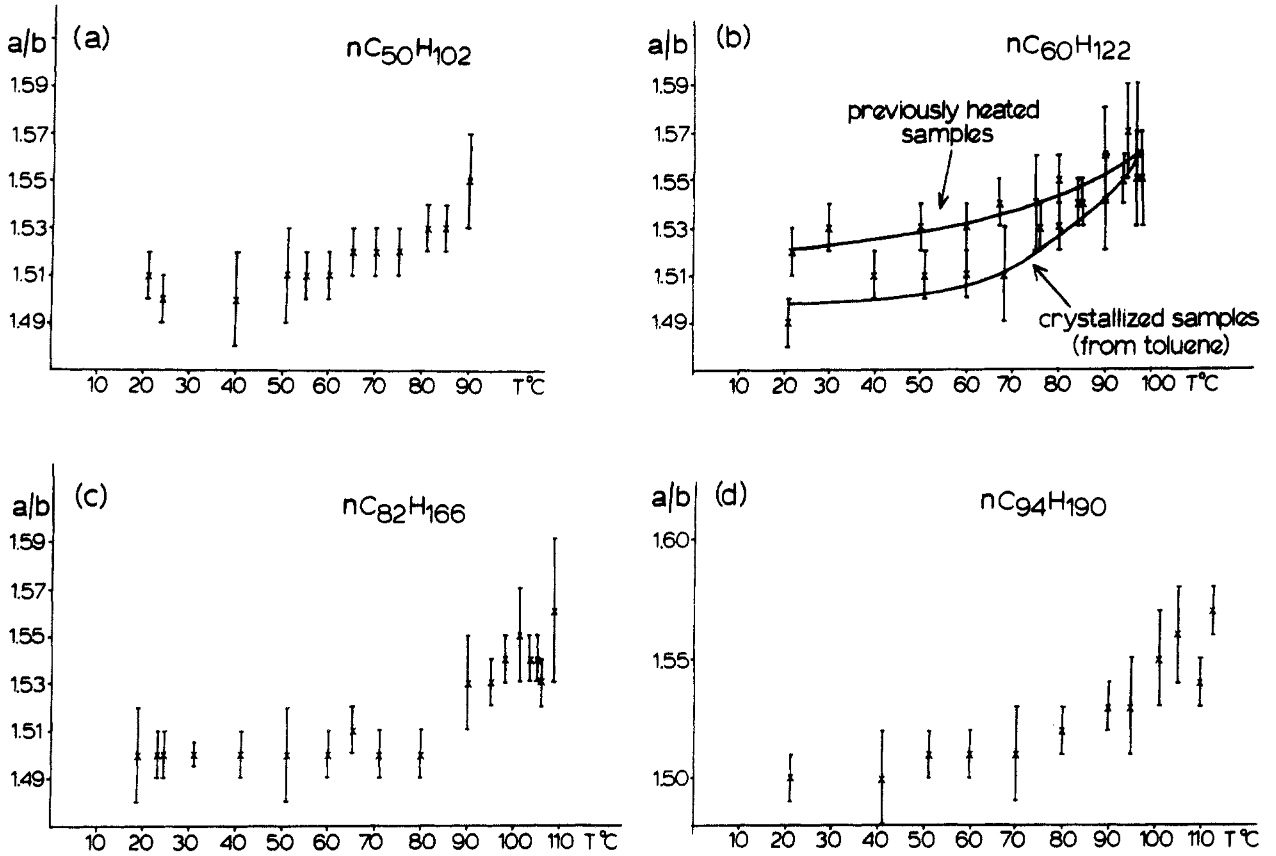

Figure 3. Plots of unit cell *a*/*b* ratios for heated paraffin lamellae: (a) *n*-$C_{50}H_{102}$ (mp 92.1 °C), (b) *n*-$C_{60}H_{122}$ (mp 99.2 °C; a second heating of the sample indicates that the inclined chain packing also expands to the previously determined end point), (c) *n*-$C_{82}H_{166}$ (mp 110.3 °C), (d) *n*-$C_{94}H_{190}$ (mp 113.8 °C).

Heating of Solution-Crystallized Paraffins. Electron diffraction patterns from solution-crystallized lamellae of these longer *n*-paraffins (Figure 2a) are typical of all such orthorhombic polymethylene layers, with cell constants near $a = 7.42$ Å and $b = 4.96$ Å. The appearance of these diffraction pattern does not change appreciably as the sample is heated toward the crystal melting point although one can see a definite gradual change in the *a*/*b* ratio with increasing temperature (Figure 3) to a limiting value around 1.55. Near the melting point it is often possible to find *hk*0 diffraction patterns (Figure 2b) which correspond to localized beginnings of oblique chain packing. The intensities of (020) spots are heightened in contrast to diminished values for the (200) and (110) reflections. Bright-field images now contain sharp bands parallel to [010] (Figure 1b) with no signs of sectorization. If the crystals are cooled to room temperature at this point, this diffraction pattern remains. Upon reheating a sample cooled from higher temperature, the plot of *a*/*b* with temperature (e.g., Figure 3b) shows that the relative increase of this axial ratio is less. Finally, if samples are crystallized from the melt, the bright-field image again resembles Figure 1b, but the diffraction pattern (Figure 2c) is readily identified as a uniform monoclinic packing for the whole crystal, characteristic of the C-form of fatty acids and other lipids.[26] This is the M_{201} structure identified earlier,[16,27] corresponding to Kitaigorodskii's[25] *R*(2,0) layer.

Heating of Epitaxially-Crystallized Paraffins. A salient expression of thermally-induced changes to the diffraction pattern is found for the orthogonal projection onto the chain axes, achieved by epitaxial orientation of, e.g., *n*-$C_{50}H_{102}$ (Figure 4). One can, for example, follow the decreasing number of orders for the 00*l* reflection in the 0*kl* diffraction pattern (Figure 5) with temperature, which is known to be associated with the chain-end disorder at the lamellar interface.[10-13] This begins to occur at temperatures where no appreciable effect on the *hk*0 reflections is noted. The effect is reversible, although incomplete recovery of the resolution for these reflections upon cooling indicates metastable surface disorder.[13]

As noted earlier in our study of binary paraffin solids,[28] it is also possible (Figure 6) to index the 01*l* reflection with the spacing of the 00*l* diffraction maxima in order to obtain the carbon number ($l = m, m + 2$) of the average chain structure in the lamellae, i.e., C_mH_{2m+2}. At low temperatures, the indices indicate that the average crystal structure is that of orthorhombic *n*-$C_{50}H_{102}$ in space group $Pca2_1$. However, at 80 °C (well before the *hk*0 diffraction pattern indicates a change from a rectangular to an oblique layer) most of the 0*kl* diffraction patterns index as if the average structure were *n*-$C_{51}H_{104}$ in space group $A2_1am$. This effect is also reversible with the *n*-$C_{50}H_{102}$ structure restored when the sample is cooled. The average lamellar spacings are (22 °C) 65.91 ± 0.72 Å and (80 °C) 66.20 ± 0.51Å compared to the respective theoretical[29] values for *n*-$C_{50}H_{102}$ (65.34 Å) and *n*-$C_{51}H_{104}$ (66.80 Å). This is the first direct observation of longitudinal chain translations in heated *n*-paraffins based on single-crystal diffraction data. It demonstrates that the lamellar thickening is due to an average change of crystal structure to that of the next longest (odd-chain) *n*-paraffin.

Discussion

As is shown above and in previous electron diffraction studies,[4] monolamellar crystals of *n*-paraffins in an untilted orthorhombic layer gradually expand to a limiting value of the unit cell ratio *a*/*b* when heated and beyond this temperature the next event depends on the chain length. However, for all examples, the heating causes conforma-

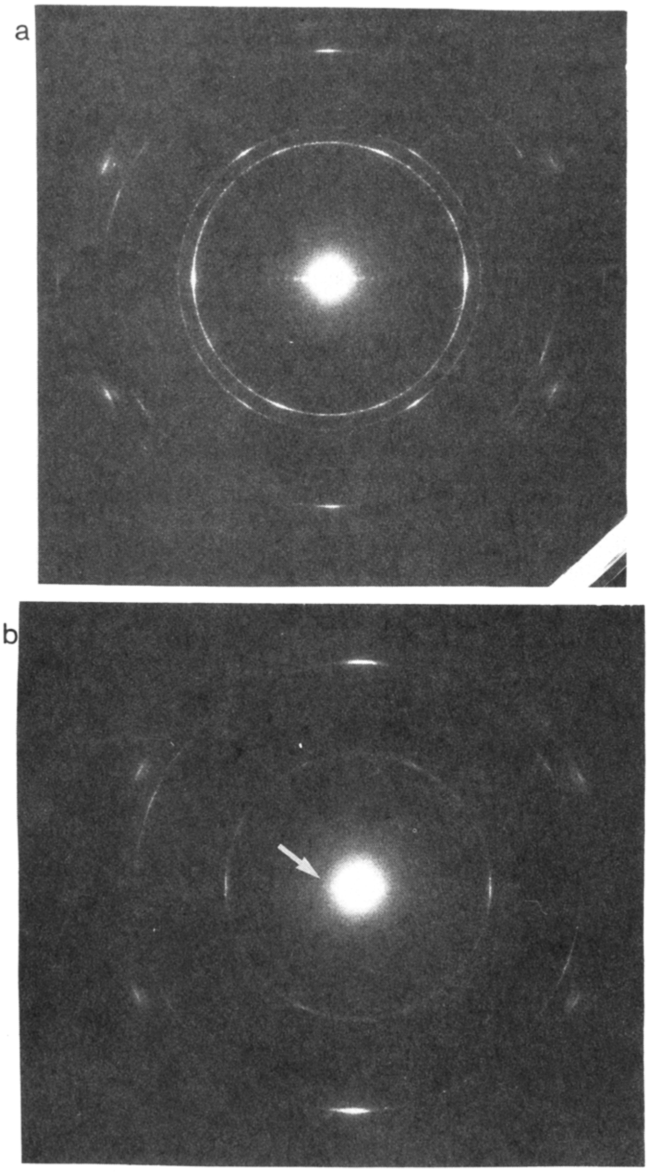

Figure 4. Electron diffraction pattern from epitaxially-oriented n-$\mathrm{C_{50}H_{102}}$: (a) at room temperature, (b) at 80 °C. Note attenuation of lamellar reflections (arrow) in the latter pattern.

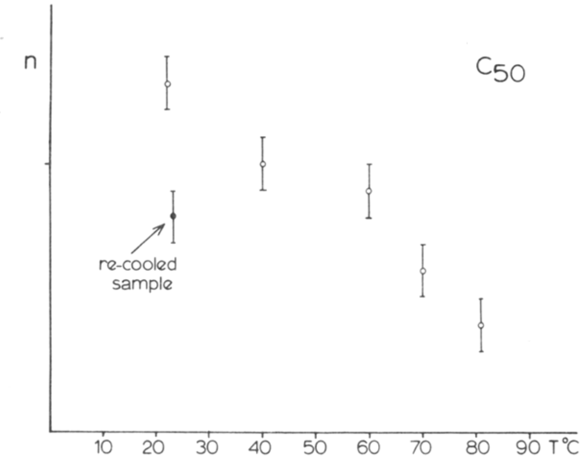

Figure 5. Plot of 00l lamellar reflection resolution as number of observed orders n for epitaxially-oriented n-$\mathrm{C_{50}H_{102}}$ heated to 80 °C and then cooled. The solid point indicates that the cooled sample has not quite recovered the interfacial order found for the original samples.

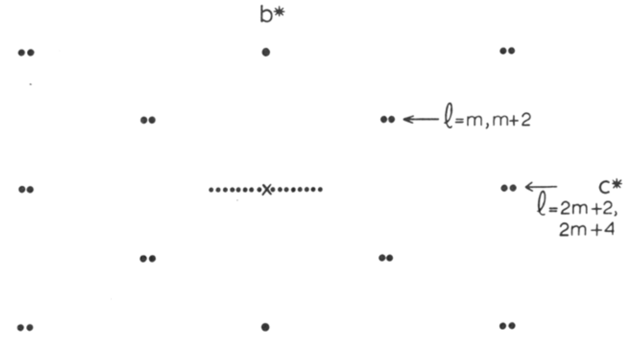

Figure 6. Use of an 0kl electron diffraction pattern from an epitaxially-oriented n-paraffin to determine the average lamellar structure. If indices of intense wide-angle 00l and 01l reflections are determined from the spacing of the low-angle 00l reflections, these l values are found to be related simply to the apparent carbon number m of the lamella n-$\mathrm{C}_m\mathrm{H}_{2m+2}$. Hence, thermal expansion of pure n-$\mathrm{C_{50}H_{102}}$ will produce an average structure which resembles n-$\mathrm{C_{51}H_{104}}$.

tional disorder to occur at the chain ends. This is directly observed by vibrational spectroscopy[6,7] and NMR[8,9] and appears in diffraction studies as changes in the low-angle 00l reflections which correspond to the lamellar interfacial disorder.[10–13]

For chain lengths within a certain dimensional limit, the next higher temperature event is the appearance of the hexagonal layer packing.[2] In some cases, e.g., n-$\mathrm{C_{36}D_{74}}$, it is not quite achieved[4] and only a rotationally-disordered orthorhombic packing is found. For the longer chains, there is a gradual change to an oblique layer packing which, beyond a certain point, is irreversible. In this study we have demonstrated for the first time that the longitudinal chain motions characteristic of this transformation begin to occur at temperatures well below the melting point, i.e., the reversible change from a n-$\mathrm{C_{50}H_{104}}$ packing to an expanded pseudo-n-$\mathrm{C_{51}H_{104}}$ structure.

The need for the longitudinal chain translations in heated paraffin layers was proposed by Maroncelli et al.[30] in their analysis of spectroscopic data to account for conformational disorder. Such longitudinal translations are also a consequence of recent molecular dynamics simulations.[31] The earlier Flory–Vrij[32] statistical mechanical calculation provides the theoretical basis for the conformational disorder of the chain-end sequences. In this calculation, the entropy gain due to the conformational disorder is considered in analyzing the fusion process. The theoretically-expected premelting temperatures are found to agree very well with the directly observed phenomena.[7–9] Direct diffraction evidence for such longitudinal chain translations has been unavailable until this single-crystal study, however, although their presence has often been inferred from morphological features of heated crystals, as mentioned. Hence, if an abrupt lattice expansion into a rotationally deformed layer is not permitted because of an excessive chain length, the longitudinal translations will provide a separate compensatory mechanism for the increased chain cross-sectional area due to conformational disorder. As yet another manifestation of this phenomenon, i.e., in mechanically-overlapped binary mixtures of n-paraffins, it has also been suggested[33,34] that long-range longitudinal chain motions are important for the spontaneous formation of the energetically-favored solid solution.

Acknowledgment. Work at Florida State University was supported by the National Science Foundation Polymers Program, Grant DMR89-14167, which is gratefully acknowledged.

References and Notes

(1) Ubbelohde, A. R. *The Molten State of Matter—Melting and Crystal Structure*; Wiley-Interscience: Chichester, U.K., 1978; pp 154–160.
(2) Ungar, G. *J. Phys. Chem.* **1983**, *87*, 689.
(3) Müller, A. *Proc. R. Soc. (London)* **1932**, *A138*, 514.
(4) Dorset, D. L. *Macromolecules* **1991**, *24*, 6521.
(5) Müller, A. *Proc. R. Soc. (London)* **1940**, *A174*, 134.
(6) Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Snyder, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 6237.
(7) Kim, Y.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1989**, *93*, 7520.
(8) Jarrett, W. L.; Mathias, L. J.; Alamo, R. G.; Mandelkern, L.; Dorset, D. L. *Macromolecules* **1992**, *25*, 3468.
(9) Möller, J.; Cantow, H. S.; Drotloff, H.; Emers, D.; Lee, K. S.; Wegner, G. *Makromol. Chem.* **1986**, *187*, 1237.
(10) Craievich, A. F.; Denicolo, I.; Doucet, J. *Phys. Rev. B* **1984**, *34*, 4782.
(11) Sullivan, P. K.; Weeks, J. J. *J. Res. Natl. Bur. Stand.* **1970**, *74A*, 203.
(12) Fischer, E. W. *Pure Appl. Chem.* **1971**, *26*, 385.
(13) Dorset, D. L.; Moss, B.; Wittmann, J. C.; Lotz, B. *Proc. Natl. Acad. Sci., U.S.A.* **1984**, *81*, 1913.
(14) Keller, A. *Philos. Mag.* **1961**, *6*, 329.
(15) Piesczek, W.; Strobl, G. R.; Malzahn, K. *Acta Crystallogr.* **1974**, *B30*, 1278.
(16) Takamizawa, K.; Ogawa, Y.; Oyama, T. *Polym. J.* **1982**, *14*, 441.
(17) Dorset, D. L.; Hu, H.; Jäger, J. *Acta Crystallogr.* **1991**, *A47*, 543.
(18) Dorset, D. L. *Macromolecules* **1990**, *23*, 623.
(19) Broadhurst, J. G. *J. Chem. Phys.* **1962**, *36*, 2578.
(20) Mandelkern, L.; Stack, G. M. *Macromolecules* **1984**, *17*, 871.
(21) Zhang, W. P.; Dorset, D. L. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1223.
(22) Dorset, D. L. *J. Macromol. Sci., Phys.* **1986**, *B25*, 1.
(23) Dorset, D. L.; Hanlon, J.; McConnell, C. H.; Fryer, J. R.; Lotz, B.; Wittmann, J. C.; Beckmann, E.; Zemlin, F. *Proc. Natl. Acad. Sci., U.S.A.* **1990**, *87*, 1696.
(24) Revol, J. F.; Manley, R. St. J. *J. Mater. Sci., Lett.* **1986**, *5*, 249.
(25) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York; 1961; p 203.
(26) Dorset, D. L.; Pangborn, W. A. *Chem. Phys. Lipids* **1982**, *30*, 1.
(27) Khoury, F. *J. Appl. Phys.* **1963**, *34*, 73.
(28) Dorset, D. L. *Macromolecules* **1987**, *20*, 2782.
(29) Nyburg, S. C.; Potworowski, J. A. *Acta Crystallogr.* **1973**, *B29*, 347.
(30) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Chem. Phys.* **1985**, *82*, 2811.
(31) Ryckaert, J.-P.; Klein, M. L.; McDonald, I. R. *Phys. Rev. Lett.* **1987**, *58*, 698.
(32) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(33) Ungar, G.; Keller, A. *Colloid. Polym. Sci.* **1979**, *257*, 90.
(34) Zerbi, G.; Piazza, R.; Moritz, K.-H. *Polymer* **1982**, *23*, 1921.
(35) Teare, P. W. *Acta Crystallogr.* **1959**, *12*, 294.
(36) Dorset, D. L. *Acta Crystallogr.* **1980**, *A36*, 592.